

# Formation of Brominated Dibenzofurans from Pyrolysis of the Polybrominated Biphenyl Fire Retardant, FireMaster FF-1

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The polybrominated biphenyl (PBB) fire retardant, FireMaster FF-1, was pyrolyzed for 20 min at 380–400°C in open glass tubes and in tubes sealed after nitrogen flushing. The pyrolyzed residue was extracted with benzene, and extracts were cleaned up on columns of graphite (Carbopack A) and alumina. Analysis was carried out by low resolution direct probe mass spectrometry (MS). Spectra from extracts of the open tube pyrolyzed material had a series of ions characteristic of tetra- and pentabrominated dibenzofurans as evidenced by comparison with spectra from 2,3,7,8-tetrabromodibenzofuran (TBDF). Confirmatory evidence for the brominated dibenzofurans was obtained by high resolution MS dual ion analysis of certain fragment and molecular ions. Recovery values of TBDF through the cleanup procedure averaged 50% and, using this recovery value and TBDF as an external standard, dual ion analyses indicated that 40 ppm tetra- and 4 ppm pentabrominated dibenzofuran were produced based on the PBB level used in the pyrolysis experiments. Additional analysis of the open tube pyrolyzed material by gas chromatography/mass spectrometry provided evidence that there was one tetrabromodibenzofuran compound with a retention time equal to that of TBDF.

Trace levels (< 1 ppm) of the molecular ion of tetrabrominated dibenzofuran were found after analysis by low resolution MS of the PBB pyrolyzed under nitrogen in sealed tubes. The experimental evidence is consistent with a mechanism for brominated dibenzofuran formation involving attack of oxygen on PBB compounds.

## Introduction

Polychlorinated dibenzofurans (PCDFs) have been identified as contaminants in a number of polychlorinated biphenyl (PCB) preparations (1–6). The PCDF compounds have also been found in PCB contaminated rice oil, the source of a severe outbreak of human illness (Yusho disease) in Japan in 1968 (7). The ratio, PCDF/PCB, in the rice oil was determined to be between 250 and 500 times higher than the same ratio for Kanechlor 400, the PCB heat transfer fluid which came into contact with the rice oil during processing (5, 6). Although to some extent the PCDFs may have concentrated in the rice oil as a result of the volatilization of lower chlorinated biphenyls, there must have been additional formation of PCDF from PCB possibly catalyzed by metals in the heat transfer tubing (6). This method of PCDF formation is supported by results from re-

cent experiments, which show that 1000 ppm of PCDF can be generated from a PCB mixture by heating for one week in an oxygen atmosphere at 300°C (8).

The polybrominated biphenyl (PBB) fire retardant FireMaster FF-1 was accidentally incorporated into animal feed in Michigan in 1973 and thousands of livestock had to be destroyed when PBB was found in their tissues (9, 10). Polybrominated dibenzofurans (PBDFs) were not found in one study (11) on the identification of trace levels of organic compounds in FireMaster FF-1. In another study (P. W. O'Keefe, unpublished work), a signal at the detection limit was found for a molecular ion of octabromodibenzofuran after analysis by high resolution mass spectrometry. However, in view of the evidence for the formation of PCDF from PCB through the action of heat, it was decided to investigate the effect of pyrolysis on the PBB fire retardant. The present paper describes experiments leading to the identification of PBDF compounds after heating FireMaster FF-1 in the temperature range 380–400°C.

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## Experimental

### Pyrolysis

FireMaster FF-1 (Michigan Chemical Company, Chicago, Ill.), 50 mg, was added to borosilicate glass tubes, 200 × 6 mm id. One tube was sealed after flushing with a slow stream of nitrogen for 5 min. Each tube was surrounded by aluminum foil packed with powdered Dry Ice, and the tubes were then heated on a sand bath for 20 min in the temperature range 380–400°C.

### Cleanup of PBB Pyrolysis Mixture

The pyrolyzed material in each tube was refluxed with 2 ml benzene for 2 min. The benzene extract was then filtered through a sodium carbonate column (40 × 6 mm) in a disposable Pasteur pipet, followed by two 5-ml benzene washings from the pyrolysis tube. The benzene was concentrated to 1 ml on a water bath. Cyclohexane (10 ml) was added, and the solvent was again evaporated to 1 ml. After two further replacements of benzene with cyclohexane, 15 ml methylene chloride was added to the flask. The extract was loaded on to a column of graphitized charcoal, Carbpac AHT (Supelco, Inc., Bellefonte, Pa.) (40 × 6 mm). Nonplanar aromatic compounds were eluted with 50 ml benzene/diethyl ether (40/60) followed by 70 ml pyridine to elute planar aromatic compounds. The pyridine fraction was diluted with 140 ml 1% HCl and extracted three times with 30-ml portions of hexane. The combined hexane fractions were washed with 100 ml water, dried over Na<sub>2</sub>SO<sub>4</sub>, and then concentrated to 1 ml. Further cleanup was carried out with an alumina column (Woelm Neutral) (40 × 6 mm) in a disposable Pasteur pipet. The alumina was activated before use by heating for 12 hr at 400°C and then cooling to room temperature in a vacuum desiccator. The first eluate, 10 ml carbon tetrachloride, was discarded, and the second eluate, 7 ml methylene chloride, was replaced with benzene using the procedure described above. For direct probe mass spectrometry fractions from the benzene solution were added to capillary tubes and the solvent was evaporated to dryness under vacuum (12).

### Direct Probe Mass Spectrometry

An AEI MS9 double-focusing mass spectrometer was used with a direct probe modified for the attachment of glass capillary tubes (12). Operating conditions were as follows: source temperature, 290°C; rhenium filament, 1.0 mA trap current; ionizing voltage, 70 eV; accelerating voltage, 8 kV;

electron multiplier, 700; internal mass marker, perfluorotributylamine (PFA); high resolution (9000) with peak scanning at 4 scans/sec and signal averaging (Varian TAC 1024 signal averaging computer); low resolution (1000) spectra were obtained with an oscillographic recorder and later converted to bar chart format by means of a PDP 8 computer.

### Gas Chromatography/Mass Spectrometry

A Perkin-Elmer model 990 gas chromatograph was coupled to a Hitachi-Perkin Elmer RMU-6L mass spectrometer by means of a low volume variable splitter followed by a porous fritted glass helium separator. The pressure reduction unit was operated at 250°C, and the split ratio was adjusted to direct 80% of the column effluent to the mass spectrometer and 20% to a flame ionization detector. The gas chromatograph was provided with a 6 ft × 1/8 in. glass column packed with 3% OVI on 100–120 mesh Gas Chrom Q. The column was temperature-programmed from 260°C (2 min) to 290°C at 6°C/min. Operating conditions for the mass spectrometer were as follows: source temperature, 210°C; ionizing potential, 70 eV; ionizing current, 100 μA; total scan time, 5.4 sec (*m/e* 30 to 739). Data acquisition and instrument control were performed on-line with an IBM 1800 computer.

## Results and Discussion

The results from direct probe low resolution mass spectrometry show that the fragmentation pattern of 2,3,7,8-tetrabromodibenzofuran (TBDF) is closely duplicated in an extract from the residue of the open tube pyrolysis of FireMaster FF-1 (Fig. 1). Ions characteristic of pentabromodibenzofuran (*m/e* 558–568, *m/e* 451–459, *m/e* 400–406) and hexabromonaphthalene (*m/e* 596–608, *m/e* 517–527, *m/e* 438–446) were also present in the spectrum from the open tube-pyrolyzed material. Molecular ions and selected fragmentation ions of the PBDF compounds were confirmed by direct probe dual ion high resolution mass spectrometry (Fig. 2 and Table 1). The levels of tetra- and pentabrominated dibenzofurans were determined from dual ion analyses to be 40 ppm and 4 ppm, respectively, by using TBDF as an external standard (Table 1). The calculations were made on the basis of a 50% recovery of TBDF through the cleanup procedure as determined in separate calibration experiments.

Additional analysis of the open tube-pyrolyzed material by gas-liquid chromatography/mass spectrometry provided evidence that there was one tetrabromodibenzofuran compound with a retention time equivalent to that of TBDF (Fig. 3) and also a

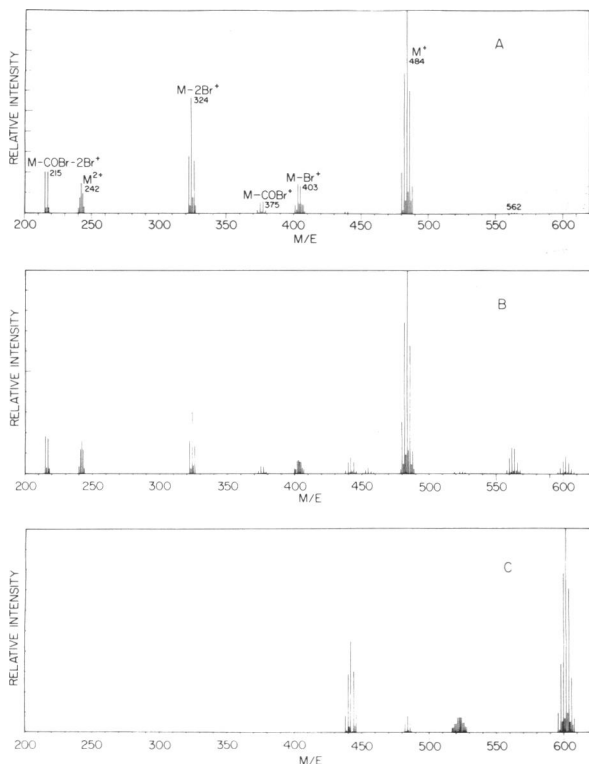


FIGURE 1. Spectra from analysis by low resolution direct probe mass spectrometry: (A) TBDF (*m/e* 215, 375, and 403 are incorrectly positioned on the spectrum; these *m/e* values refer to peaks two units lower in mass); (B) cleaned-up extract from the open tube pyrolysis of FireMaster FF-1; (C) cleaned-up extract from the pyrolysis of FireMaster FF-1 under nitrogen.

pentabromodibenzofuran and a hexabromonaphthalene whose substitution patterns could not be identified due to the lack of standard compounds.

When FireMaster FF-1 was pyrolyzed in a nitrogen atmosphere, it was found after analysis by low-resolution direct-probe mass spectrometry that hexabromonaphthalene was the only compound present at a detectable level in the cleaned up extract (Fig. 1C). Weak signals for the molecular ion isotopes of TBDF were also apparent in the spectrum. By comparison with the low resolution direct probe spectrum of TBDF, the approximate levels of hexabromonaphthalene were calculated as 3 ppm

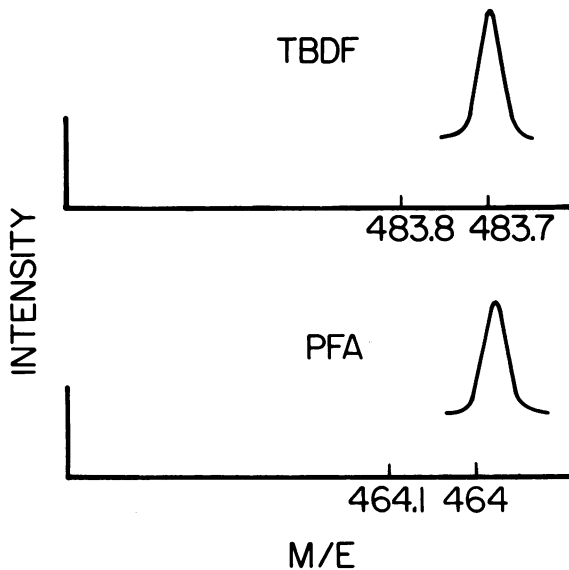


FIGURE 2. Analysis by dual ion direct probe high resolution mass spectrometry of a cleaned-up extract from the open tube pyrolysis of FireMaster FF-1. Exact mass determination of a TBDF molecular ion by reference to a PFA ion.

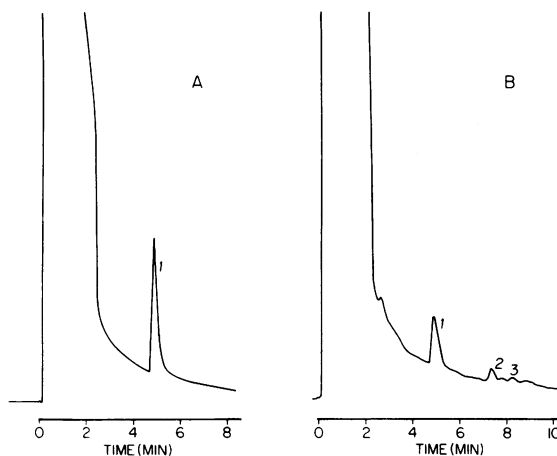


FIGURE 3. Analysis by gas chromatography/mass spectrometry. Gas chromatogram from 20% of column effluent for (A) TBDF and (B) a cleaned-up extract from the open tube pyrolysis of Firemaster FF-1. Peak identification from mass spectra: (1) TBDF, (2) hexabromonaphthalene, and (3) pentabromodibenzofuran.

Table 1. Results from analysis by high resolution direct probe mass spectrometry of extracts from FireMaster FF-1 pyrolyzed in open tubes.

	Mass determinations						Quantitation, ppm <sup>a</sup>
	Molecular ion (M <sup>+</sup> )		M-COBr		M <sup>2+</sup>		
	Calcd	Anal.	Calcd	Anal.	Calcd	Anal.	
Tetrabromodibenzofurans	483·6954	483·695	374·7842	374·784	241·8477	241·848	40
Pentabromodibenzofurans	561·6059	561·606	454·6926	454·693			4

<sup>a</sup> Corrected for a 50% recovery of TBDF through the cleanup procedure.

and 6 ppm in the FireMaster FF-1 pyrolyzed, respectively, in an open tube and in a tube containing a nitrogen atmosphere. Since hexabromonaphthalene was previously identified as a contaminant of FireMaster FF-1 at levels of 25 ppm or greater (P. W. O'Keefe, unpublished work; 11), it is apparent that the compound was not completely degraded under the conditions used in the pyrolysis experiments.

The role of oxygen in the formation of the PBDF from pyrolysis of the PBB fire retardant is supported by comparable experiments carried out with a PCB formulation (6). It was suggested in the case of the PCB experiments that the PCDF compounds could be formed by the replacement of two *ortho* chlorine atoms on each aromatic ring by an oxygen atom or alternatively by an attack of oxygen at an unsubstituted *ortho* position to form a chlorinated hydroxybiphenyl which could then eliminate HCl to form a PCDF compound. Since 2,2',4,4',5,5'-hexabromobiphenyl is the major brominated biphenyl isomer in FireMaster FF-1 and the related product FireMaster BP-6 (11, 13-15), the former mechanism could explain the formation of TBDF in the open tube pyrolysis experiments.

Dibenzo-*p*-dioxin and dibenzofuran substituted with chlorine atoms in 2, 3, 7, and 8 positions exhibit potent toxic properties (7), and therefore it is possible that TBDF may prove to be equally toxic. Although PBB compounds are no longer marketed as fire retardants in the United States, approximately 12 million pounds were produced between 1970 and 1974, mainly for incorporation into the plastic components of certain electrical appliances and business machines (16). These products will eventually be discarded when they become obsolescent and, if they are incinerated, burning conditions will require careful control in order to avoid the formation of PBDF compounds. Similar considerations would apply to the disposal of animal tissues contaminated with PBB residues as a result of environmental accidents, such as occurred in Michigan.

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